

PATENT SPECIFICATION

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(54) PROCESS FOR PREPARING PAPER FROM LAUAN PULP

(71) We, MITSUBISHI CORPORATION, a Japanese corporation, of No. 6—3, 2-chome, Marunouchi, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:

This invention relates to a process for preparing paper from a lauan hardwood pulp containing resin.

Lauan is the generic name for numerous species of tropical hardwoods found in substantial amounts in many countries of Southeast Asia. Due to an ever increasing shortage of pulpwood in those areas, there is a great interest and need to use lauan wood as a source of papermaking fibre. Lauan wood, however, is not readily pulped by conventional means due to a high content of unsaponifiable resins. Pulp prepared from lauan hardwood have been found to contain resin particles ranging in size from microscopic to 400 microns size and larger. These resin particles make it very difficult to manufacture paper and especially a high quality paper. For instance a paper mill in the Phillipines reportedly has to clean its paper machine twice a day due to resin accumulation and clogging of screens. Other processing problems also are encountered. Paper quality is adversely affected because the tropical lauan hardwoods contain resin and pitch. Reportedly DAMAR resin is found in lauan hardwood pulps. Upon processing of lauan hardwoods by known conventional pulping and paper-making methods and techniques, the resultant paper is of low quality and of an inferior grade such as generally to be non-acceptable to the printing trade. The inferior quality of this paper results because of an excessive resin or pitch content therein. The conventionally prepared paper has a nonuniform surface in that resin or pitch particles therein create a quite noticeable irregular surface of the nature of numerous "pimples" or the like protruding therefrom. A method for preparation of an improved paper from lauan pulps and of a paper of substantially uniform appearance significantly free from a "pimpled" appearance provides a highly desirable, important, and significant advance in the paper making art.

Ultrasonic energy and irradiation of various materials is known in the art for various purposes. Many effects are known to be able to be produced by ultrasonic energy. These include emulsification of immiscible liquids, accelerated dispersion of solids into liquids, acceleration of chemical reactions, and the like. Ultrasonic vibrations on both native and regenerated cellulose fibers reportedly breaks them down into thin transparent "fibrils" (Textile Research Journal, August, 1950, pages 549—555); cotton fibres subjected to ultrasonic irradiation leads to fiber surface modifications, fiber entanglements, and fibrillation, but does not seem to be promising for trash removal from raw cotton (Textile Research Journal, August, 1967, pages 621—633); ultrasonics can function as a disintegrating agent on the biological structure of wood (Journal of Polymer Science, Vol. VI, No. 4, pages 503—507); highly hydrated degasified fibers can be provided by ultrasonic irradiation of bleached sulphite paper pulp (British Patent No. 796,932); passage of an ultrasonic beam has been used for inspection and supervision of continuous lye-washing or digestion in paper pulp preparation (U.S. Patent No. 3,611,793); the thickness, consistency, and homogeneity of pulp suspension in the forming wire of a paper machine are determinable by using ultrasonic energy (U.S. Patent No. 3,442,756); a combined centrifugal and ultrasonic treatment of waste paper removes impurities therefrom as a scum (German Patent 1,030,670, May 22, 1958);

and reportedly one can avoid undesirable coagulation and foam formation caused by resin impurities in the paper mill by the action of ultrasonic waves on paper pulps in the screening unit of the paper machine prior to sheet formation (German Auslegeschrift No. 1,185,468, January 14, 1965). In this latter mentioned reference, apparently the resin impurities therein for the most part tend to deposit on the fibers or fiber bundles making them sticky and tending to agglomerate. It is important and decisive in the process in this German patent that the resin particles be loosened from the fibers and be finely distributed in the pulp by an ultrasonic treatment imposed where the pulp leaves the head box, or damming position, and passes onto the screening table to reach the dewatering screen.

According to the present invention there is provided a process for preparing paper from a lauan hardwood pulp containing resin, comprising the steps of:

(a) preparing an aqueous suspension of a sulphate pulp of said hardwood having at least 20% active alkali (as defined herein) during digestion of the hardwood;

(b) subjecting the prepared aqueous suspension of sulphate pulp while of consistency of less than 2 per cent to ultrasonic treatment at a frequency between 15 kHz and 1 MHz at an intensity of at least 3 watts/cm² for at least one minute; and

(c) subsequently making a paper from the aqueous suspension of sulphate pulp subjected to step (b).

Inherent in the method of the invention are a combination of elements characterising the ultrasonic treatment process of the invention. The preceding paragraph sets forth the major portion of the combined elements in so far as they establish a threshold for application of the invention's process to provide improved paper from lauan pulp. However, to progress from slight improvement to significant improvement the parameters and values alter for the various elements which in combination characterise the process of the invention. For example, the resin particles can be reduced to finer size and any resin content of the produced paper further diminished with a corresponding further increase in paper surface smoothness realised upon the active alkali factor being about 25 or greater in the digestion of the lauan hardwood and with the ultrasonic treating at a frequency between 15 and 60 kHz, an intensity between 3 and 15 watts/cm², and for at least two minutes.

Still greater improvements are provided in the produced paper and the paper making process facilitated when the invention's ultrasonic treating process is applied to the precedingly described prepared sulphate pulp after it has been converted to a bleached pulp and is of a consistency of less than 1 percent. Preferably for optimising the paper improvement the precedingly described process of ultrasonic treating is of the aqueous bleached sulphate pulp of a consistency of about 0.5 percent or less and the paper also is made from the ultrasonically treated pulp while also of a consistency of about 0.5 percent or less.

For a better understanding of the present invention and to show more clearly how it may be carried into effect reference will now be made, by way of example, to the accompanying drawings in which:

FIGURE 1 is an enlarged photograph showing a portion of a paper handsheet formed from lauan hardwood pulp which has been subjected to the ultrasonic method of the invention; and

FIGURE 2 is an enlarged photograph showing a portion of a paper handsheet formed from a lauan hardwood pulp which has not been processed according to the invention.

The enlargement in both FIGURES 1 and 2 is about two times. Comparison of these photographic figures shows that the untreated pulp produces a paper (FIG. 2) in which a nonuniform surface appearance of pimple-like protuberances readily is visible to the unaided eye. To provide a ready comparison by the eye of the amount of improvement in step-wise gradations of paper smoothness, there is used in the disclosure what are designated "Resin Dispersion Ratings" of 1 = no improvement; 2 = slight improvement; 3 = moderate improvement; and 4 = significant improvement. Under these resin dispersion ratings, the paper shown in FIG. 1 has a resin dispersion rating of 4 and the untreated or control paper shown in FIG. 2 has a resin dispersion rating of 1.

With reference in particular to FIG. 1, the illustrated portion of a paper handsheet is from a hereafter described 2nd bleached A lauan wood pulp (note Table 2) which as a 0.44 percent consistency pulp had been subjected to an ultrasonic treatment of 15 watt/cm² for 5 minutes prior to preparing a handsheet therefrom as hereafter described. With reference in particular to FIG. 2, the

illustrated portion of a paper handsheet is from a 2nd bleached A lauan wood pulp of 0.44 percent consistency which, as hereafter described, had been processed into a handsheet and which had not been subjected to any ultrasonic treatment prior to forming the handsheet therefrom.

5 To exemplify practice of the invention, two different tropical lauan hardwoods 5
were prepared in chip size for subsequent laboratory size preparations of several
bleached and unbleached pulps therefrom. The first lauan wood once believed to
be *Shorea leprasula* wood, subsequently later was identified definitely as
10 *Hoperfolia Sym Meranti Merah* wood, and herein is referred to as 30049—1—4 or 10
lauan A. The chips of this lauan wood, as obtained, did not exceed in size about 1.5
in. in maximum dimension. The second lauan wood was a red lauan wood, *Shorea*
Negrosensis Foxw, which herein is referred to as 30817—37—0 or lauan B. It was
obtained as rough lumber and subsequently chipped to chips of a size not
15 exceeding about 0.75 in. in maximum dimension. Both lauan woods A and B had no 15
visible bark content therein.

In general, the sulfate or kraft process was employed for providing pulp
preparations from these two lauan woods. For preparation of unbleached pulps,
generally 4000 grams (oven-dry weight basis) of lauan chips were placed in an
appropriate size digester or cooker; there were added compounds to achieve a
20 desired% active alkali and % sulfidity (as defined hereinafter); and then a requisite 20
amount of additional water was added, with allowance made for water constituting
moisture content of the chips and water in the aqueous solutions of the added
active alkali chemicals, to provide a desired liquor to wood ratio, generally 4 to 1.
25 Thereupon the contents of the digester were brought to appropriate cooking 25
temperature and cooked for the requisite time following which the cooked
contents were "blown" with liquor drained from the digester. The cooked and
blown fibrous pulp then was water washed and passed through a coarse screen to
remove shives therefrom.

30 Throughout the disclosure effort has been made to use descriptive terminology 30
recognized and conventional to the particular art of concern. For example in the
sulfate pulping process, illustrative terminology and accepted definitions therefor
include:

$$\% \text{ active alkali} = \frac{\text{NaOH and Na}_2\text{S} \text{ (expressed as equivalent Na}_2\text{O)} \times 100}{\text{wt. of dry wood}}$$

$$\% \text{ sulfidity} = \frac{\text{Na}_2\text{S}}{\text{NaOH} + \text{Na}_2\text{S}} \times 100 \text{ (all chemicals expressed as Na}_2\text{O)}$$

35 shives = small bundles of fibers not completely separated during preparation of the 35
paper pulp.

Unless expressly stated or defined otherwise, descriptive terms and
terminology used throughout this disclosure and the claims are intended to connote
their standard recognized meanings to those skilled in the art to which they pertain.
40 At various places throughout the abbreviation TAPPI is used, which stands for 40
Technical Association of the Pulp and Paper Industry, whose mailing address is 1
Dunwoody Park, Atlanta, Georgia 30341, U.S.A., with TAPPI generally used in
conjunction with a Code No. to designate a specific standard, suggested method, or
test procedure, or the like, which has received recognition by the membership of
45 said TAPPI, is available in printed form in a manual from TAPPI, and is accepted 45
as standard through the art and industry.

The following TABLE I presents data on cooking conditions and results of
cooks for preparations from lauan woods A and B of several unbleached pulps
employed in illustrating practices of the invention.

TABLE 1
PREPARATIONS OF UNBLEACHED PULPS

Lauan Wood Designation	A	A	B	B
Unbleached Pulp Designation	1st	2nd	2nd	3rd (a)
Cook No.	30049- 18-1	32274- 15-2	32274- 15-1	30817-37-1 30817-37-2
Quantity of Wood, grams (b)	4000	4000	4000	4000
Active Alkali (%)	25	25	25	20
Sulfidity (%)	25	25	25	25
Liquor:Wood Ratio	4:1	4:1	4:1	4:1
100 C to 170 C, min (c)	90	90	90	90
Time at 170 C, min	75	75	75	90
Residuals (as gpl Na ₂ O)				
Na ₂ S	8.7	10.23	8.06	4.34
NaOH	8.8	8.37	18.29	5.27
Total	17.5	18.60	26.35	9.61
Permanganate No.	15.1	15.8	14.35	18.9
Yield %				
Screened	36.4	38.41	46.49	49.09
Shives	0.5	0.28	0.27	0.25
Total	36.9	38.68	46.76	49.34

(a) Cook Nos. 30817-37-1 and 30817-37-2 blended together provide unbleached 3rd Pulp (30817-37-3) of lauan wood B.

(b) Oven-dried basis.

(c) Time elapsed in raising temperature from 100 C to 170 C.

For preparations of bleached pulps from lauan woods A and B, there are employed portions of those unbleached pulps reported in TABLE 1. A CEDED (chlorine, alkaline extraction, chlorine dioxide; alkaline extraction, chlorine dioxide) sequence was used to bleach these unbleached lauan wood pulps.

The following TABLE 2 presents data of specific bleaching conditions, residuals, yields, and final brightness for the prepared bleached pulps subsequently employed in illustrating practices of the invention.

TABLE 2

PREPARATIONS OF BLEACHED PULPS

Lauan Wood Designation	A	A	B	B
Bleached Pulp Designation	1st	2nd	2nd	3rd
Bleach No.	30049- 35-1	32274- 16-2	32274- 16-1	30817- 38-3
Unbleached Stock Pulp	30049- 18-1	32274- 15-2	32274- 15-1	30817- 37-3
Permanganate No.	15.1	15.8	14.35	—
<u>Chlorination</u>				
Demand, %	70	70	70	70
Cl ₂ Applied, %	5.31	5.60	5.07	6.23
Consistency, %	3	3	3	3
Time, min	60	60	60	60
Temp, C	26	24	25	25
Residual, pH	1.9	1.95	2.0	1.8
<u>Extraction</u>				
NaOH Applied, %	3.0	3.0	3.0	3.0
Consistency, %	12	12	12	12
Time, min	120	120	120	120
Temp, C	65	68	68	65
Residual, pH	10.8	10.8	10.4	10.6
Permanganate No.	3.1	3.6	3.25	2.4
<u>Chlorine Dioxide</u>				
ClO ₂ Applied, %	1.2	1.2	1.2	0.8
Time, min	150	150	150	150
Temp, C	83	80	80	83
Consistency, %	12	12	12	12
Residual, pH	2.2	2.3	2.2	2.1
Brightness	73.2	78	84	76.3-78.2

TABLE 2 (continued)

<u>Extraction</u>				
NaOH Applied, %	1.0	1.0	1.0	1.0
Time, min	120	120	120	120
Temp, C	65	67	67	65
Consistency, %	12	12	12	12
Residual, pH	10.9	10.5	10.5	10.8
<u>Chlorine Dioxide</u>				
ClO ₂ Applied, %	0.6	0.6	0.6	0.4
Time, min	240	240	240	240
Temp, C	83	83	84	83
Consistency, %	12	12	12	12
Residual, pH	2.6	2.4	2.5	2.9
<u>Sulphur Dioxide Stabilization</u>				
Consistency, %	3	3	3	
SO ₂ Addition, %	0.2	0.2	0.2	
Final pH	2.9	2.9	2.8	
Final Brightness	85.0	86.7	90.1	93.11-93.28
Bleached Yield (% based on unbleached pulp)	94.5	93.46	93.48	
Bleached Yield (% based on wood)	34.87	35.90	43.46	

- 5 Ultrasonics as used herein defines acoustical waves occurring above the audible range of frequencies. Any suitable device equipped with means for imparting high frequency vibrations to a liquid can be employed to subject the aqueous paper pulp to ultrasonic treatment. Acoustic type generators, such as the piezoelectric type or the magnetostrictive type, can be used. For example, a quartz oscillator, which is energized by an alternating current generator or a magnetic coil working upon a membrane, illustrate means useful for generating the ultrasonic high frequency vibrations employed in the invention. Useful vibration frequency can be as low as 15,000 c.p.s. (cycles per second) and as high as 1,000,000 c.p.s. and at any of the various frequencies therebetween. Preferably the employed frequency is between 15 and 60 kHz. 5
- 10 For laboratory practice of the invention, there is used a high frequency sound wave generating means, which comprises a 2400 watt Cavitron model ultrasonic generator and magnetostrictive transducer driving a 1.5 inch flanged horn, of known utility for dispersion preparations with this means driven at high amplitudes producing flow and radiation patterns in the pulp conducive to producing uniform dispersions while simultaneously emulsifying resin in water. Ideally the applied ultrasonics reduces the size of resin particles in the paper pulp to that of colloiddally dispersed resin particles so that resin removal occurs in the washing and/or in the 10
- 15 20 15 20

water passing through the paper-forming screen with conventional pulp washing techniques and conventional paper making.

Illustrative useful operating conditions for the just-described ultrasonic generating means, when treating paper pulp of 0.44% and 0.5% consistency are: power input — 15 watts/cm²; plate current — 0.5 ampere; bias current — 17 amperes; and application times of at least 1 minute and generally about 5 minutes.

For evaluation of the effect of various parameters, techniques and the like of the invention's ultrasonic method on the paper pulp, there are prepared paper handsheets in the laboratory. These handsheets are prepared using a British Standard Sheet Mold and the procedure described in TAPPI Standard Method T-205-os-71, "Forming Handsheets for Physical Tests in Pulp." The handsheet preparation procedure involves collecting the fibers from a pulp slurry, and also any large size and undispersed resin present, on a screen while the water portion of the pulp slurry and dispersed fine resin particles pass through the screen. The produced finished handsheets approximate 6 to 6 $\frac{1}{4}$ in. diameter. In preparing each sheet there is employed an amount of aqueous pulp suspension to provide a handsheet of about 1.2 grams dry weight. Generally the employed aqueous pulp is of 0.44 percent consistency with about 275 ml. thereof employed. In some instances pulps of 0.5 percent consistency are employed. Paper handsheets are prepared from each of the unbleached (Table 1) and bleached (Table 2) A and B lauan wood pulps after ultrasonic treatments. For control and comparison purposes, paper handsheets also are prepared of the unbleached (Table 1) and bleached (Table 2) A and B lauan wood pulps, which pulps are used as prepared for making the paper handsheets and without any ultrasonic treatment of the pulp.

The following TABLE 3 presents exemplifying data on the precedingly described prepared bleached and unbleached pulps of the A and B lauan woods, and includes various ultrasonic treatments of these pulps along with Resin Dispersion Ratings of handsheets prepared from the ultrasonically treated lauan pulps. The tabular data presented includes: identifying pulp designation description and number; and ultrasonic treating conditions of power input or intensity, treatment time, temperature of pulp slurry before and after treatment; and pulp consistency during ultrasonic treating.

TABLE 3
ULTRASONICALLY TREATED PULPS

Pulp Designation	Base Pulp Number	Intensity, watt/cm ²	Temp. of Slurry, F		Pulp Consistency, %	Resin Dispersion Rating (a)
			Treatment Time, min	Before Treatment	After Treatment	
3rd Unbleached B lauan	30817-37-3	15	5	57	178	1-2
3rd Bleached B lauan	30817-38-3	"	5	69	178	3-4
2nd Unbleached B lauan	32274-15-1	"	5	68	186	1-2
2nd Unbleached A lauan	-15-2	"	5	68	187	3-4
2nd Bleached B lauan	-16-1	"	5	68	185	3-4
2nd Bleached A lauan	-16-2	"	5	69	185	4
2nd Unbleached A lauan	-15-2	"	2.5	70	149	3
2nd Bleached A lauan	32274-16-2	"	0.5	68	87	1
Ditto	Ditto	"	1.0	68	105	2
"	"	"	2.0	68	136	3-4
"	"	"	3.0	68	158	4
"	"	"	4.0	68	175	4
"	"	"	5.0	68	190	4
"	"	"	5.0	68	195	2
"	"	"	5.0	68	195	1
3rd Unbleached B lauan (b)	30817-37-3	"	5.0	68	182	1-2

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(54) PROCESS FOR PREPARING PAPER FROM LAUAN PULP

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This invention relates to a process for preparing paper from a lauan hardwood pulp containing resin.

Lauan is the generic name for numerous species of tropical hardwoods found in substantial amounts in many countries of Southeast Asia. Due to an ever increasing shortage of pulpwood in those areas, there is a great interest and need to use lauan wood as a source of papermaking fibre. Lauan wood, however, is not readily pulped by conventional means due to a high content of unsaponifiable resins. Pulps prepared from lauan hardwood have been found to contain resin particles ranging in size from microscopic to 400 microns size and larger. These resin particles make it very difficult to manufacture paper and especially a high quality paper. For instance a paper mill in the Phillipines reportedly has to clean its paper machine twice a day due to resin accumulation and clogging of screens. Other processing problems also are encountered. Paper quality is adversely affected because the tropical lauan hardwoods contain resin and pitch. Reportedly DAMAR resin is found in lauan hardwood pulps. Upon processing of lauan hardwoods by known conventional pulping and paper-making methods and techniques, the resultant paper is of low quality and of an inferior grade such as generally to be non-acceptable to the printing trade. The inferior quality of this paper results because of an excessive resin or pitch content therein. The conventionally prepared paper has a nonuniform surface in that resin or pitch particles therein create a quite noticeable irregular surface of the nature of numerous "pimples" or the like protruding therefrom. A method for preparation of an improved paper from lauan pulps and of a paper of substantially uniform appearance significantly free from a "pimpled" appearance provides a highly desirable, important, and significant advance in the paper making art.

Ultrasonic energy and irradiation of various materials is known in the art for various purposes. Many effects are known to be able to be produced by ultrasonic energy. These include emulsification of immiscible liquids, accelerated dispersion of solids into liquids, acceleration of chemical reactions, and the like. Ultrasonic vibrations on both native and regenerated cellulose fibers reportedly breaks them down into thin transparent "fibrils" (Textile Research Journal, August, 1950, pages 549—555); cotton fibres subjected to ultrasonic irradiation leads to fiber surface modifications, fiber entanglements, and fibrillation, but does not seem to be promising for trash removal from raw cotton (Textile Research Journal, August, 1967, pages 621—633); ultrasonics can function as a disintegrating agent on the biological structure of wood (Journal of Polymer Science, Vol. VI, No. 4, pages 503—507); highly hydrated degasified fibers can be provided by ultrasonic irradiation of bleached sulphite paper pulp (British Patent No. 796,932); passage of an ultrasonic beam has been used for inspection and supervision of continuous lye-washing or digestion in paper pulp preparation (U.S. Patent No. 3,611,793); the thickness, consistency, and homogeneity of pulp suspension in the forming wire of a paper machine are determinable by using ultrasonic energy (U.S. Patent No. 3,442,756); a combined centrifugal and ultrasonic treatment of waste paper removes impurities therefrom as a scum (German Patent 1,030,670, May 22, 1958);

and reportedly one can avoid undesirable coagulation and foam formation caused by resin impurities in the paper mill by the action of ultrasonic waves on paper pulps in the screening unit of the paper machine prior to sheet formation (German Auslegeschrift No. 1,185,468, January 14, 1965). In this latter mentioned reference, apparently the resin impurities therein for the most part tend to deposit on the fibers or fiber bundles making them sticky and tending to agglomerate. It is important and decisive in the process in this German patent that the resin particles be loosened from the fibers and be finely distributed in the pulp by an ultrasonic treatment imposed where the pulp leaves the head box, or damming position, and passes onto the screening table to reach the dewatering screen.

According to the present invention there is provided a process for preparing paper from a lauan hardwood pulp containing resin, comprising the steps of:

(a) preparing an aqueous suspension of a sulphate pulp of said hardwood having at least 20% active alkali (as defined herein) during digestion of the hardwood;

(b) subjecting the prepared aqueous suspension of sulphate pulp while of consistency of less than 2 per cent to ultrasonic treatment at a frequency between 15 kHz and 1 MHz at an intensity of at least 3 watts/cm² for at least one minute; and

(c) subsequently making a paper from the aqueous suspension of sulphate pulp subjected to step (b).

Inherent in the method of the invention are a combination of elements characterising the ultrasonic treatment process of the invention. The preceding paragraph sets forth the major portion of the combined elements in so far as they establish a threshold for application of the invention's process to provide improved paper from lauan pulp. However, to progress from slight improvement to significant improvement the parameters and values alter for the various elements which in combination characterise the process of the invention. For example, the resin particles can be reduced to finer size and any resin content of the produced paper further diminished with a corresponding further increase in paper surface smoothness realised upon the active alkali factor being about 25 or greater in the digestion of the lauan hardwood and with the ultrasonic treating at a frequency between 15 and 60 kHz, an intensity between 3 and 15 watts/cm², and for at least two minutes.

Still greater improvements are provided in the produced paper and the paper making process facilitated when the invention's ultrasonic treating process is applied to the precedingly described prepared sulphate pulp after it has been converted to a bleached pulp and is of a consistency of less than 1 percent. Preferably for optimising the paper improvement the precedingly described process of ultrasonic treating is of the aqueous bleached sulphate pulp of a consistency of about 0.5 percent or less and the paper also is made from the ultrasonically treated pulp while also of a consistency of about 0.5 percent or less.

For a better understanding of the present invention and to show more clearly how it may be carried into effect reference will now be made, by way of example, to the accompanying drawings in which:

FIGURE 1 is an enlarged photograph showing a portion of a paper handsheet formed from lauan hardwood pulp which has been subjected to the ultrasonic method of the invention; and

FIGURE 2 is an enlarged photograph showing a portion of a paper handsheet formed from a lauan hardwood pulp which has not been processed according to the invention.

The enlargement in both FIGURES 1 and 2 is about two times. Comparison of these photographic figures shows that the untreated pulp produces a paper (FIG. 2) in which a nonuniform surface appearance of pimple-like protuberances readily is visible to the unaided eye. To provide a ready comparison by the eye of the amount of improvement in step-wise gradations of paper smoothness, there is used in the disclosure what are designated "Resin Dispersion Ratings" of 1 = no improvement; 2 = slight improvement; 3 = moderate improvement; and 4 = significant improvement. Under these resin dispersion ratings, the paper shown in FIG. 1 has a resin dispersion rating of 4 and the untreated or control paper shown in FIG. 2 has a resin dispersion rating of 1.

With reference in particular to FIG. 1, the illustrated portion of a paper handsheet is from a hereafter described 2nd bleached A lauan wood pulp (note Table 2) which as a 0.44 percent consistency pulp had been subjected to an ultrasonic treatment of 15 watt/cm² for 5 minutes prior to preparing a handsheet therefrom as hereafter described. With reference in particular to FIG. 2, the

illustrated portion of a paper handsheet is from a 2nd bleached A lauan wood pulp of 0.44 percent consistency which, as hereafter described, had been processed into a handsheet and which had not been subjected to any ultrasonic treatment prior to forming the handsheet therefrom.

To exemplify practice of the invention, two different tropical lauan hardwoods were prepared in chip size for subsequent laboratory size preparations of several bleached and unbleached pulps therefrom. The first lauan wood once believed to be *Shorea leprasula* wood, subsequently later was identified definitely as *Hoperfiolia Sym Meranti Merah* wood, and herein is referred to as 30049—1—4 or lauan A. The chips of this lauan wood, as obtained, did not exceed in size about 1.5 in. in maximum dimension. The second lauan wood was a red lauan wood, *Shorea Negrosensis* Foxw, which herein is referred to as 30817—37—0 or lauan B. It was obtained as rough lumber and subsequently chipped to chips of a size not exceeding about 0.75 in. in maximum dimension. Both lauan woods A and B had no visible bark content therein.

In general, the sulfate or kraft process was employed for providing pulp preparations from these two lauan woods. For preparation of unbleached pulps, generally 4000 grams (oven-dry weight basis) of lauan chips were placed in an appropriate size digester or cooker; there were added compounds to achieve a desired % active alkali and % sulfidity (as defined hereinafter); and then a requisite amount of additional water was added, with allowance made for water constituting moisture content of the chips and water in the aqueous solutions of the added active alkali chemicals, to provide a desired liquor to wood ratio, generally 4 to 1. Thereupon the contents of the digester were brought to appropriate cooking temperature and cooked for the requisite time following which the cooked contents were "blown" with liquor drained from the digester. The cooked and blown fibrous pulp then was water washed and passed through a coarse screen to remove shives therefrom.

Throughout the disclosure effort has been made to use descriptive terminology recognized and conventional to the particular art of concern. For example in the sulfate pulping process, illustrative terminology and accepted definitions therefor include:

$$\% \text{ active alkali} = \frac{\text{NaOH and Na}_2\text{S} \text{ (expressed as equivalent Na}_2\text{O)} \times 100}{\text{wt. of dry wood}}$$

$$\% \text{ sulfidity} = \frac{\text{Na}_2\text{S}}{\text{NaOH} + \text{Na}_2\text{S}} \times 100 \text{ (all chemicals expressed as Na}_2\text{O)}$$

shives = small bundles of fibers not completely separated during preparation of the paper pulp.

Unless expressly stated or defined otherwise, descriptive terms and terminology used throughout this disclosure and the claims are intended to connote their standard recognized meanings to those skilled in the art to which they pertain. At various places throughout the abbreviation TAPPI is used, which stands for Technical Association of the Pulp and Paper Industry, whose mailing address is 1 Dunwoody Park, Atlanta, Georgia 30341, U.S.A., with TAPPI generally used in conjunction with a Code No. to designate a specific standard, suggested method, or test procedure, or the like, which has received recognition by the membership of said TAPPI, is available in printed form in a manual from TAPPI, and is accepted as standard through the art and industry.

The following TABLE 1 presents data on cooking conditions and results of cooks for preparations from lauan woods A and B of several unbleached pulps employed in illustrating practices of the invention.

TABLE 1
PREPARATIONS OF UNBLEACHED PULPS

Lauan Wood Designation	A	A	B	B	
Unbleached Pulp Designation	1st	2nd	2nd	3rd (a)	
Cook No.	30049- 18-1	32274- 15-2	32274- 15-1	30817-37-1 30817-37-2	
Quantity of Wood, grams (b)	4000	4000	4000	4000	4000
Active Alkali (%)	25	25	25	20	20
Sulfidity (%)	25	25	25	25	25
Liquor:Wood Ratio	4:1	4:1	4:1	4:1	4:1
100 C to 170 C, min (c)	90	90	90	90	90
Time at 170 C, min	75	75	75	90	90
<u>Residuals (as gpl Na₂O)</u>					
Na ₂ S	8.7	10.23	8.06	4.34	4.34
NaOH	8.8	8.37	18.29	5.27	5.58
Total	17.5	18.60	26.35	9.61	9.92
Permanganate No.	15.1	15.8	14.35	18.9	15.6
<u>Yield %</u>					
Screened	36.4	38.41	46.49	49.09	48.65
Shives	0.5	0.28	0.27	0.25	0.15
Total	36.9	38.68	46.76	49.34	48.80

(a) Cook Nos. 30817-37-1 and 30817-37-2 blended together provide unbleached 3rd Pulp (30817-37-3) of lauan wood B.

(b) Oven-dried basis.

(c) Time elapsed in raising temperature from 100 C to 170 C.

For preparations of bleached pulps from lauan woods A and B, there are employed portions of those unbleached pulps reported in TABLE 1. A CEDED (chlorine, alkaline extraction, chlorine dioxide; alkaline extraction, chlorine dioxide) sequence was used to bleach these unbleached lauan wood pulps.

The following TABLE 2 presents data of specific bleaching conditions, residuals, yields, and final brightness for the prepared bleached pulps subsequently employed in illustrating practices of the invention.

TABLE 2
PREPARATIONS OF BLEACHED PULPS

Lauan Wood Designation	A	A	B	B
Bleached Pulp Designation	1st	2nd	2nd	3rd
Bleach No.	30049— 35—1	32274— 16—2	32274— 16—1	30817— 38—3
Unbleached Stock Pulp	30049— 18—1	32274— 15—2	32274— 15—1	30817— 37—3
Permanganate No.	15.1	15.8	14.35	—
<u>Chlorination</u>				
Demand, %	70	70	70	70
Cl ₂ Applied, %	5.31	5.60	5.07	6.23
Consistency, %	3	3	3	3
Time, min	60	60	60	60
Temp, C	26	24	25	25
Residual, pH	1.9	1.95	2.0	1.8
<u>Extraction</u>				
NaOH Applied, %	3.0	3.0	3.0	3.0
Consistency, %	12	12	12	12
Time, min	120	120	120	120
Temp, C	65	68	68	65
Residual, pH	10.8	10.8	10.4	10.6
Permanganate No.	3.1	3.6	3.25	2.4
<u>Chlorine Dioxide</u>				
ClO ₂ Applied, %	1.2	1.2	1.2	0.8
Time, min	150	150	150	150
Temp, C	83	80	80	83
Consistency, %	12	12	12	12
Residual, pH	2.2	2.3	2.2	2.1
Brightness	73.2	78	84	76.3—78.2

TABLE 2 (continued)

<u>Extraction</u>				
NaOH Applied, %	1.0	1.0	1.0	1.0
Time, min	120	120	120	120
Temp, C	65	67	67	65
Consistency, %	12	12	12	12
Residual, pH	10.9	10.5	10.5	10.8
<u>Chlorine Dioxide</u>				
ClO ₂ Applied, %	0.6	0.6	0.6	0.4
Time, min	240	240	240	240
Temp, C	83	83	84	83
Consistency, %	12	12	12	12
Residual, pH	2.6	2.4	2.5	2.9
<u>Sulphur Dioxide Stabilization</u>				
Consistency, %	3	3	3	
SO ₂ Addition, %	0.2	0.2	0.2	
Final pH	2.9	2.9	2.8	
Final Brightness	85.0	86.7	90.1	93.11-93.28
Bleached Yield (% based on unbleached pulp)	94.5	93.46	93.48	
Bleached Yield (% based on wood)	34.87	35.90	43.46	

- 5 Ultrasonics as used herein defines acoustical waves occurring above the audible range of frequencies. Any suitable device equipped with means for imparting high frequency vibrations to a liquid can be employed to subject the aqueous paper pulp to ultrasonic treatment. Acoustic type generators, such as the piezoelectric type or the magnetostrictive type, can be used. For example, a quartz oscillator, which is energized by an alternating current generator or a magnetic coil working upon a membrane, illustrate means useful for generating the ultrasonic high frequency vibrations employed in the invention. Useful vibration frequency can be as low as 15,000 c.p.s. (cycles per second) and as high as 1,000,000 c.p.s. and at any of the various frequencies therebetween. Preferably the employed frequency is between 15 and 60 kHz. 5
- 10 For laboratory practice of the invention, there is used a high frequency sound wave generating means, which comprises a 2400 watt Cavitron model ultrasonic generator and magnetostrictive transducer driving a 1.5 inch flanged horn, of known utility for dispersion preparations with this means driven at high amplitudes producing flow and radiation patterns in the pulp conducive to producing uniform dispersions while simultaneously emulsifying resin in water. Ideally the applied ultrasonics reduces the size of resin particles in the paper pulp to that of colloiddally dispersed resin particles so that resin removal occurs in the washing and/or in the 10
- 15 20

water passing through the paper-forming screen with conventional pulp washing techniques and conventional paper making.

Illustrative useful operating conditions for the just-described ultrasonic generating means, when treating paper pulp of 0.44% and 0.5% consistency are: power input — 15 watts/cm²; plate current — 0.5 ampere; bias current — 17 amperes; and application times of at least 1 minute and generally about 5 minutes.

For evaluation of the effect of various parameters, techniques and the like of the invention's ultrasonic method on the paper pulp, there are prepared paper handsheets in the laboratory. These handsheets are prepared using a British Standard Sheet Mold and the procedure described in TAPPI Standard Method T-205-os-71, "Forming Handsheets for Physical Tests in Pulp." The handsheet preparation procedure involves collecting the fibers from a pulp slurry, and also any large size and undispersed resin present, on a screen while the water portion of the pulp slurry and dispersed fine resin particles pass through the screen. The produced finished handsheets approximate 6 to 6 $\frac{1}{4}$ in. diameter. In preparing each sheet there is employed an amount of aqueous pulp suspension to provide a handsheet of about 1.2 grams dry weight. Generally the employed aqueous pulp is of 0.44 percent consistency with about 275 ml. thereof employed. In some instances pulps of 0.5 percent consistency are employed. Paper handsheets are prepared from each of the unbleached (Table 1) and bleached (Table 2) A and B lauan wood pulps after ultrasonic treatments. For control and comparison purposes, paper handsheets also are prepared of the unbleached (Table 1) and bleached (Table 2) A and B lauan wood pulps, which pulps are used as prepared for making the paper handsheets and without any ultrasonic treatment of the pulp.

The following TABLE 3 presents exemplifying data on the precedingly described prepared bleached and unbleached pulps of the A and B lauan woods, and includes various ultrasonic treatments of these pulps along with Resin Dispersion Ratings of handsheets prepared from the ultrasonically treated lauan pulps. The tabular data presented includes: identifying pulp designation description and number; and ultrasonic treating conditions of power input or intensity, treatment time, temperature of pulp slurry before and after treatment; and pulp consistency during ultrasonic treating.

TABLE 3
ULTRASONICALLY TREATED PULPS

Pulp Designation	Base Pulp Number	Intensity, watt/cm ²	Temp. of Slurry, F		Pulp Consistency, %	Resin Dispersion Rating (a)
			Treatment Time, min	Before Treatment	After Treatment	
3rd Unbleached B lauan	30817-37-3	15	5	57	178	1-2
3rd Bleached B lauan	30817-38-3	"	5	69	178	3-4
2nd Unbleached B lauan	32274-15-1	"	5	68	186	1-2
2nd Unbleached A lauan	-15-2	"	5	68	187	3-4
2nd Bleached B lauan	-16-1	"	5	68	185	3-4
2nd Bleached A lauan	-16-2	"	5	69	185	4
2nd Unbleached A lauan	-15-2	"	2.5	70	149	3
2nd Bleached A lauan	32274-16-2	"	0.5	68	87	1
Ditto		"	1.0	68	105	2
"	"	"	2.0	68	136	3-4
"	"	"	3.0	68	158	4
"	"	"	4.0	68	175	4
"	"	"	5.0	68	190	4
"	"	"	5.0	68	195	2
"	"	"	5.0	68	195	1
3rd Unbleached B lauan (b)	30817-37-3	"	5.0	68	182	1-2

TABLE 3 (continued)

Pulp Designation	Base Pulp Number	Intensity, watt/cm ²	Treatment Time, min.	Temp. of Slurry, F		Pulp Consistency, %	Resin Dispersion Rating (a)
				Before Treatment	After Treatment		
2nd Bleached B lauan	32274-16-1	.3	5	70	100	5	3-4
Ditto	Ditto	6	5	69	139	"	3-4
"	"	9	5	69	166	"	3-4
2nd Bleached A lauan	32274-16-2	3	5	69	100	"	1-2
Ditto	Ditto	6	5	69	135	"	1-2
"	"	9	5	69	164	"	3-4
3rd Bleached B lauan	30817-38-3	3	5	69	107	"	3-4
Ditto	Ditto	6	5	69	131	"	3-4
"	"	9	5	70	162	"	3-4

(a) 1 = no improvement; 2 = slight improvement; 3 = moderate improvement; 4 = significant improvement (paper handsheet).

(b) Aging study: pulp was aged for 10 days at 105 C prior to ultrasonic treatment.

A close examination of the data presented in TABLE 3 for the various pulps of the two exemplary lauan woods reveals the following important and significant elements and characteristics of the method of the invention:

(a) Effect of Pulp Consistency.

For the 2nd bleached A lauan wood pulp, where ultrasonic treating conditions are held constant, one requires a pulp consistency of 2 percent during ultrasonic treating to show slight improvement and a pulp consistency of 1 percent and less to provide significant improvement in surface smoothness of paper prepared from the ultrasonically treated pulp. An especially preferred pulp consistency is about 0.5 percent. At 5 percent pulp consistency, no improvement is observed.

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(b) Ultrasonic Power Input.

For the 2nd and 3rd bleached B lauan wood pulps, power inputs of 3, 6, and 9 watt/cm² provide substantially the same paper surface improvement of moderate to significant. Conversely the 2nd bleached A lauan wood pulp (a different lauan wood with the same pulping and bleaching treatment) requires a power input or ultrasonic intensity of 9 watts/cm² to provide significant improvement in paper smoothness. However, if only a slight improvement is desired, 3 watts/cm² suffices for the 2nd bleached A lauan wood pulp. Desirably for economic operation one will employ a power input just slightly above the threshold intensity requisite to treat the pulp of the particular lauan wood so that it will provide a paper of the desired smoothness quality. Generally the useful power input is between about 3 and 15 watts/cm².

(c) Ultrasonic Treatment Time.

For the 2nd bleached A lauan wood pulp, when other ultrasonic treating conditions are held constant, it is apparent that at least one minute of ultrasonic treating is necessary to provide a slight improvement. Desirably at least two minutes of ultrasonic treating is employed to provide moderate to significant improvement in paper surface smoothness with at least a three minute treatment time preferred.

(d) Age of Treated Pulp.

Although presented data is very cursory in nature with only one aged pulp being ultrasonically treated and that being for a limited accelerated aging of 10 days at 105 C, indications are that aging does not enhance or detract from the smoothness of paper made from the ultrasonically treated 3rd unbleached B lauan wood pulp.

(e) Pulp Temperature For Ultrasonic Treatment.

Although not tabulated in TABLE 3, ultrasonic treatments of the 3rd unbleached B lauan wood commencing with treatment of the pulp at a near freezing temperature (34°F) and at a near boiling temperature (191°F) do not appear to favour nor detract from action of the ultrasonic treatment. Likewise, as apparent from the TABLE 3 pulps subjected to varied increased power inputs, increasing temperatures during treatment of the ultrasonically treated pulp also appear not to favor nor detract from the paper surface improvement obtainable by practice of the invention.

Additional elements and characteristics of the ultrasonic pulp treatment of the invention include:

(f) Pulp Slurry pH.

A series of pulps of various pH were prepared from the 3rd unbleached B lauan wood pulp by adding sulfuric acid or sodium hydroxide thereto to provide pulps of 2.8, 7.1, 8.6, and 10.8 pH. These pulps of different pH subsequently were subjected to ultrasonic treatment and paper handsheets prepared therefrom. Visual observation failed to detect any noticeable effect on the surface quality of the prepared paper handsheets when the pulp slurry pH differed.

(g) Adding Surfactant to Pulp.

A series of experiments were conducted with the 3rd unbleached B lauan wood pulp to which various surfactants in various amounts were admixed prior to ultrasonic treating at a power input of 15 watts/cm² for 5 minutes. The employed surfactants included a variety of chemical structures of the nonionic and anionic types and included a series of various surfactants having increasing HLB numbers from 2 upward to 18. The HLB of a surfactant (e.g. emulsifier) is a numerical expression of the size and strength of its "Hydrophile-Lipophile Balance." That is, it is an expression of the size and strength of the hydrophilic (water loving or polar) and lipophilic groups (oil-loving or nonpolar) present in emulsifier molecule. Emulsifiers with low HLB numbers are more lipophilic and vice versa as one proceeds to emulsifiers with high HLB numbers. HLB numbers for surfactants are well recognized in the art, such as illustrated by "HLB: An Explanation and a Bibliography" by Paul Becher and William C. Griffin, 1974/Detergents and Emulsifiers/North American, pages 227 et seq. and the 265 papers listed in the bibliography. With the particular unbleached lauan wood pulp of concern only a few nonionic emulsifiers and those of low HLB, i.e. of 6 and lower HLB and most desirably of about 2 HLB and

lower HLB number, appeared to offer any promise as additives to be present during ultrasonic treatment to favourably influence and improve the surface smoothness quality of paper prepared from ultrasonically treated unbleached pulp containing these low HLB nonionic emulsifiers. The improvement obtained is marginal and often inconsistent in that not all apparently replicate experiments will show improvement. Particularly useful as such emulsifier additives to the pulp are sorbitan trioleate (available as Span (Registered Trade Mark) 85 from ICI America, Inc.) which has an HLB number of 2.1, and sorbitan tristearate (available as Span (Registered Trade Mark) 65 from ICI America, Inc.) which has an HLB number of 1.8. Useful amounts include from 5 to 20 percent by weight of such low HLB nonionic emulsifier, based on the fibers in the paper pulp, (or alternatively about 0.02 percent by weight based on the total weight (water plus fibers, etc.) of the aqueous pulp) with pulps of consistencies less than 1 percent and generally about 0.5 percent.

(h) % Active Alkali for Sulfate Pulps

With reference to Table 1 it can be noted therefrom that in the sulfate pulping process employed to provide both the 3rd unbleached and 3rd bleached B lauan wood pulps that the % active alkali is 20% in contrast to all of the other pulps of the A and B lauan woods described in Tables 1 and 2 wherein the % active alkali is 25% in their pulping. A review of the Resin Dispersion Ratings in Table 3 for papers prepared from these B lauan wood pulps whose % active alkali was 20%, and especially the papers made from the 3rd unbleached B lauan wood pulp, indicates only marginal to slight improvement in paper surface quality from such pulps after ultrasonic treating. There possibly exists a lower limit of 20% for the active alkali during the sulfate pulping process with higher % active alkali essential, and particularly required with certain species of lauan wood to obtain significant improvements in paper surface quality.

To better illustrate and characterize the nature of and amount of resin found in various pulps, several of the prepared lauan wood pulps were extracted with a 50:50 parts by volume mixture of hexane : methanol. The amount of extracted resin was measured and infrared analysis made of the extracted resin along with DTA (Differential Thermal Analysis) to determine the resin's degradation temperature. The following TABLE 4 presents data on the amount of resin found to be present and the DTA-determined degradation temperature of the extracted resin for several pulps so characterized.

TABLE 4

CHARACTERIZATION DATA

Pulp Designation	Base Pulp Number	Percent Resin (a)	DTA (b)
			Temperature, C
3rd unbleached B lauan	30817-37-3	2.55	36.7
3rd bleached B lauan	30817-38-3	1.50	51.6
1st bleached A lauan	30049-35-1	3.20	75.0

(a) By 50:50 hexane/methanol extraction.

(b) Differential Thermal Analysis.

Significant observations from the data of Table 4 are that the resin content will and does vary from one species to another species of lauan wood. Note that the A lauan pulp contains over twice as much resin as the B lauan pulp corresponding thereto. Also to be noted are visual differences in the extracted resins from the two different lauan wood pulps. Resin extracted from the A lauan wood pulp was dry white/yellow, and powdery in appearance. Resin from the unbleached B lauan wood pulp was more of a brown, sticky, and pitch-like material. While the resin of

the bleached B lauan wood pulp was generally similar to that extracted from the unbleached B lauan wood pulp, it appeared not to be quite as sticky.

No glass transition points were noted in the differential thermal analysis (DTA) with it apparent therefrom that the resins are not crystalline in nature. The difference, or increase in degradation temperature, upon proceeding from the unbleached to bleached B lauan pulp suggests that the bleaching of the pulp likely alters the resin so that it degrades at a higher temperature than in a corresponding unbleached pulp.

Infrared analysis of the resins from the pulps tabulated in Table 4 provides indications of chemical differences of the various extracted resins. Qualitatively the resins from the bleached A and B lauan woods were found to be similar. Both contained a mixture of carbonyl types (acids and esters predominate), long-chain hydrocarbons, and some hydroxyl groups (some of which were thought to be water in the resin sample). The ratios of the various components varied with the resin from the bleached A lauan pulp containing more hydroxyl, while the resin from the bleached B lauan pulp contained more carbonyl and more long-chain hydrocarbons. The resin from the unbleached B lauan pulp exhibited most of the same components as the other two resins except its carbonyl components exhibited a higher ratio of ester to acid and also a higher ratio of long-chain hydrocarbons than the two resins from bleached pulps. Additionally this latter resin from the unbleached B lauan pulp contained some aliphatic unsaturation, not noted in the other two resins, and also the presence of sizable amounts of metal carboxylates. The infrared analysis results further confirm that bleaching of the sulfate pulp of a lauan wood resin significantly changes the chemical structure of the resin. This correlates very well with applicant's preferred practice of the ultrasonic treatment of lauan resin pulp in that the preferred practice is of a bleached sulfate lauan wood pulp for easier processing and for providing significant improvement in surface smoothness of paper made therefrom.

Quantitative determinations of the resin content were made of resin in paper handsheets prepared from several prepared lauan pulp and the same pulps after being ultrasonically treated at an intensity of 15 watts/cm² for 5 minutes. The resins in these handsheets were extracted using a 50:50 by volume ethanol : hexane mixture by refluxing the handsheet directly in the mixture for six hours. Because of the small amounts of resin for extraction numerous extraction controls were run to identify possible statistical error in the extraction technique. As a result of such control data and using a statistical "t" value approach, the below reported extraction data is considered valid with 95 percent confidence. The control paper handsheet made from the 2nd bleached B lauan wood pulp was found to contain 1.50% by weight resin, while the paper made from the ultrasonically treated 2nd bleached B lauan wood pulp failed to provide a measurable amount of resin within the limits of the employed determination technique. Correspondingly the control paper handsheet from the 2nd bleached A lauan wood pulp was found to contain 2.00% by weight of resin, while the paper made from the ultrasonically treated 2nd bleached A lauan pulp failed to provide a measurable amount of resin within the limits of the employed technique.

Effort was made to evaluate smoothness of various prepared handsheets by a quantitative measurement means analogous to the aforescribed visual subjective resin dispersion rating. Reasoning behind a possible quantitative determination was that in control paper handsheets the paper's surface includes numerous small protuberances thereon obviously from its resin particle content and thus exhibits a rough paper surface. In this quantitative smoothness determination effort, there was used a Bendsten Smoothness and Porosity Tester-Model 5 (Manufactured by Anderson and Sorenson, Copenhagen, Denmark) with this tester modified to use a 75 manostate weight (weight which results in an air pressure corresponding to a 75 mm water column) and a 200 g weight on its smoothness gauge. This tester quantitatively measures air flow through the smoothness gauge/paper interface. The rate of air flow increases as the paper surface increases in roughness. Smoothness measurements were made on the felt side of prepared handsheets made from prepared lauan pulps which had and had not been subjected to ultrasonic treatment. The 2nd unbleached A lauan pulp provided a Bendsten smoothness value of 428 ml. of air from the control handsheet compared to 228 ml of air for the handsheet from the ultrasonically treated pulp. Handsheet of the same ultrasonically treated 2nd unbleached A lauan pulp earlier exhibited a Resin Dispersion Rating of 3—4. Correspondingly the 2nd bleached A lauan provided a control handsheet of Bendsten smoothness of 404 ml. of air compared to a

5 handsheet of the same pulp after ultrasonic treatment which gave a Bendsten smoothness of 288 ml. of air (earlier Resin Dispersion Rating 4). The 2nd bleached B lauan pulp provided a control handsheet recording a Bendsten smoothness of 264 ml. of air compared to the comparable pulp after ultrasonic treatment providing a handsheet of Bendsten smoothness of 206 ml. of air (earlier Resin Dispersion Ratio 3—4). The 2nd unbleached B lauan pulp provided a control handsheet exhibiting a Bendsten smoothness of 208 ml. of air compared to the same pulp after ultrasonic treating producing a handsheet having a Bendsten smoothness of 193 (earlier Resin Dispersion Ratio 1—2). The 3rd unbleached and bleached B lauan pulps provided control handsheets and after ultrasonic treatment provided handsheets which upon comparison of the exhibited Bendsten smoothness values therefore failed to agree with earlier subjectively determined Resin Dispersion Ratio values for such handsheets and in this respect the Bendsten smoothness tester failed to provide quantitative data on smoothness of value to the present invention. Why the attempted quantitative Bendsten smoothness tester failed with this particular lauan pulp to agree with earlier determined Resin Dispersion Ratios is unknown with the measured Bendsten smoothness values being about the same magnitude for both control handsheets and handsheets from ultrasonically treated pulps.

20 Tensile tests were made on paper handsheets made from various of the prepared pulps including pulps subjected to ultrasonic treatment and the same pulps not ultrasonically treated. The tensile measurements were conducted using a Table Model Instron (Registered Trade Mark) Tester, a jaw gap of 10 cm., a jaw speed of 2.54 cm/min, and a paper sample size 14 cm. x 1.5 cm with the paper samples conditioned overnight at 73°F and 50 percent relative humidity prior to testing. Papers made from the ultrasonically treated (15 watts/cm² for 5 min.) 3rd unbleached B lauan pulp, 2nd bleached B lauan pulp, and 2nd bleached A lauan pulp all exhibited considerable increased tensile strengths (about two-fold tensile strength increases) in comparison to their control papers from pulps not ultrasonically treated. However, noticeable decreased tensile strengths were observed for papers made from lesser ultrasonically treated (at least than 15 watts/cm² and at 3, 6, and 9 watts/cm² for 5 min.) pulps indicating a threshold level of ultrasonic treating parameters exists for concurrently increasing tensile strength along with providing paper of improved surface quality. Of interest is that inclusion of about 6 percent by weight based on the fiber content of a surfactant of HLB No. 2 in the ultrasonic treated 3rd unbleached B lauan wood pulp resulted in a much lower tensile strength paper than from the same ultrasonically treated pulp not containing surfactant with the observed tensile strength closely approximating the strength of the control paper. Thus, while inclusion of a surfactant of HLB of about 2 in a lauan pulp can aid in providing paper of improved appearance, the surfactant's inclusion can be at the expense of not obtaining paper of increased tensile strength.

45 While the foregoing exemplary disclosure of ultrasonic treating of lauan hardwood pulps has been illustrated as applying the ultrasonics directly to the aqueous lauan sulphate paper pulps in its unbleached and bleached pulp states, it is to be recognized that this invention contemplates application of ultrasonic treating may, at least for some species of lauan woods, more favorably be at intermediate pulp and paper making steps and locations, such as at the digester or cooker, during one or more of the bleaching steps, during pulp washing (either before or after bleaching or both), during beating, refining, and the like intermediate steps and locations.

WHAT WE CLAIM IS:—

1. A process for preparing paper from a lauan hardwood pulp containing resin, comprising the steps of:
 - 55 (a) preparing an aqueous suspension of a sulphate pulp of said hardwood having at least 20% active alkali (as defined herein) during digestion of the hardwood;
 - (b) subjecting the prepared aqueous suspension of sulphate pulp while of consistency of less than 2 percent to ultrasonic treatment at a frequency between 15 kHz and 1MHz at an intensity of at least 3 watts/cm² for at least one minute; and
 - 60 (c) subsequently making a paper from the aqueous suspension of sulphate pulp subjected to step (b).
2. A process according to claim 1, wherein the sulphate pulp has at least 25% active alkali during digestion.

3. A process according to claim 1 or 2, wherein the ultrasonic treatment is at a frequency between 15 kHz and 60 kHz.
4. A process according to claim 1, 2 or 3, wherein the ultrasonic treatment is at an intensity between 3 watts/cm² and 15 watts/cm².
- 5 5. A process according to any preceding claim, wherein the ultrasonic treatment is for at least two minutes. 5
6. A process according to claim 5, wherein the ultrasonic treatment is for at least three minutes.
7. A process according to any preceding claim, wherein the aqueous sulphate pulp is converted to a bleached pulp prior to step (b). 10
- 10 8. A process according to any preceding claim, wherein the consistency of the pulp in step (b) is less than 1 percent. 10
9. A process according to claim 8, wherein the consistency of the pulp in step (b) is less than 0.5 percent.
- 15 10. A process for preparing paper according to claim 1 and substantially as hereinbefore described with reference to the accompanying drawings. 15
11. Paper made by a process according to claim 1 and substantially as hereinbefore described.

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1 SHEET

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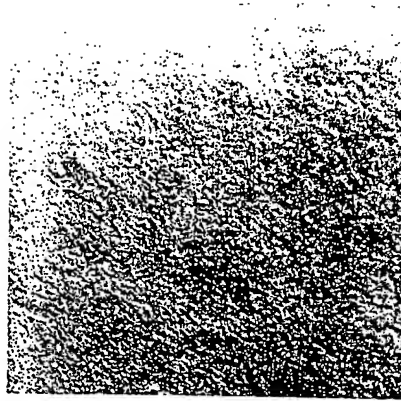


Fig.1

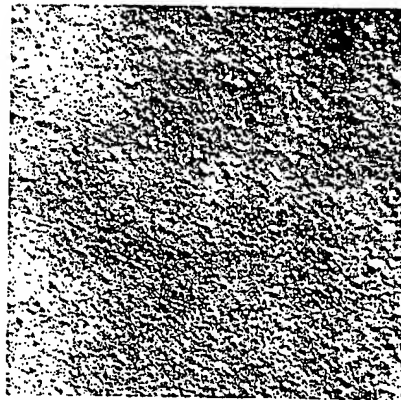


Fig.2

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